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STRUCTURAL STUDIES OF NONTRONITES WITH DIFFERENT IRON CONTENTS BY ^{57}Fe MÖSSBAUER SPECTROSCOPY

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Abstract—The ^{57}Fe Mössbauer spectra of a series of untreated and Ca-saturated nontronites showed a predominant Fe^{3+} resonance which was computer-fitted with two Fe^{3+} doublets defining iron in non-equivalent cis-$FeO_4(OH)_2$ octahedral sites. In most spectra a doublet indicating tetrahedral Fe^{3+} was fitted and in one untreated sample a doublet indicating interlayer Fe^{3+} was identified. In a further untreated sample the interlayer iron was present as Fe^{2+}. Upon Ca-saturation the interlayer iron was displaced. It also appears that the interlayer iron was present in at least two different interlayer sites. From the computer-fitted data it was clear that the interlayer cations have a significant effect on the Mössbauer resonances of iron in the two non-equivalent cis-octahedral and the tetrahedral sites of nontronite.

Key Words—Interlayer cation, Iron, Mössbauer spectroscopy, Nontronite, Structural sites.

INTRODUCTION

In recent years the Mössbauer spectrum of nontronite (idealized composition = $(Ca_{0.5},Na)_{0.66}Fe^{3+}{}_4(Si,Al)_8O_{20}(OH)_4 \cdot nH_2O$) has been studied by a number of workers. Goodman *et al.* (1976) and Rozenson and Heller-Kallai (1977) initially suggested that the two Fe^{3+} doublets which could be computer-fitted to the experimental broad Fe^{3+} resonance may be attributed to Fe^{3+} in the octahedral $FeO_4(OH)_2$ sites with both the cis- and trans-arrangement of OH groups. Goodman *et al.* (1976) also identified an additional less intense doublet which they assigned to Fe^{3+} replacing (Si,Al) in the tetrahedral sites. Inasmuch as the electron diffraction work of Mering and Oberlin (1967), now confirmed by Besson *et al.* (1983a), showed the trans-sites to be vacant, Goodman (1978) suggested that the presence of Fe^{3+} in the tetrahedral sites could generate two distinct environments for the cis-octahedral sites, consistent with the computer-fitted Mössbauer spectrum. In addition, Johnston and Cardile (1985a) showed that for untreated, Ca- and K-saturated nontronite from Garfield, Washington (GAR), the parameter values for these two computer-fitted octahedral Fe^{3+} doublets displayed a marked dependence on the nature of the interlayer cation. They suggested that the electrostatic interactions from both the interlayer cations and nearby tetrahedral Fe^{3+} ions could give rise to these two distinct electric-field gradients within neighboring cis-$FeO_4(OH)_2$ sites. They also showed for such samples that if the χ^2 value is used as a measure of the goodness of the computer-fit, the spectra should be recorded to a background count of preferably greater than 3×10^6. The resulting χ^2 value then reflects both the validity of the structural model used and the extent of disorder within the structure.

In the present paper these ideas have been extended and the role of the interlayer cation has been elucidated by means of a similar study of six nontronites from different locations and of different compositions.

EXPERIMENTAL

The locations of the nontronites and their structural formula calculated in a conventional manner are presented in Table 1. Both the untreated and Ca-saturated samples of the Bingham Canyon, Utah (BIN); Manito, Washington (MAN); and Spokane County, Washington (SPO), nontronites, together with the Ca-saturated Woody, California (WOD), Li-saturated Panamint Valley, California (CAL), and Na-saturated Koegas, South Africa (KOE), nontronites were used.

The cation-saturation procedure (e.g., for Ca) consisted of shaking 0.5 g of the clay with 10 ml of 1 M $CaCl_2$ solution for 10–15 minutes. The supernatant liquid was decanted and this process repeated several times. The sample was then washed repeatedly by shaking with water and centrifuging until the wash water was free of Cl^- ions (by Ag^+ test). The clay was then dried at room temperature.

^{57}Fe Mössbauer spectra were recorded at room temperature unless otherwise stated using an ELSCINT AME40C spectrometer and a ^{57}Co source in a rhodium matrix. The velocity scale was calibrated with reference to natural iron, with the midpoint of the iron hyperfine spectrum defining zero velocity. The spectra were computer-fitted to a number of Lorentzian peak lineshapes using a non-linear regression χ^2 minimization procedure. To achieve convergence, it was generally nec-

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Table 1. Locations and compositions of nontronites.

Location		Wt. % Fe	Composition per $O_{10}(OH)_2$
[1]Bingham Canyon, Utah	(BIN)	20.05	$(Ca_{0.259}K_{0.009})(Si_{3.491}Al_{0.509})(Al_{0.426}Fe_{1.455}Mg_{0.138}Ti_{0.016})$
[2]Panamint Valley, California	(CAL)	34.95	$(Si_{3.10}Al_{0.07}Fe_{0.83})(Fe_{2.02}Mg_{0.11})$
[2]Koegas, Cape Province, S.A.	(KOE)	33.39	$(Si_{3.31}Al_{0.04}Fe_{0.66})(Fe_{2.03}Mg_{0.05})$
[1]Manito, Washington	(MAN)	25.06	$(Ca_{0.250})(Si_{3.500}Al_{0.500})(Al_{0.142}Fe_{1.821}Mg_{0.049}Mn_{0.004})$
[1]Spokane County, Washington	(SPO)	29.20	$(Ca_{0.232})(Si_{3.700}Al_{0.034}Fe_{0.266})(Fe_{1.924}Mg_{0.029}Mn_{0.004})$
[1,3]Woody, California	(WOD)	28	

[1] Supplied with analyses by K. Norrish, Division of Soils, C.S.I.R.O., Adelaide. Analyses are for the Ca-saturated samples.
[2] Supplied by B. A. Goodman, The Macaulay Institute for Soil Research, Aberdeen. Composition from Table 1 of Goodman *et al.* (1976).
[3] This actual nontronite composition could not be determined as the sample was associated with approximately 30% silica. The Fe content was determined by assuming the SiO_2 content of the nontronite to be equal to the mean of the other samples (see text).

essary to constrain the widths and dips of corresponding pairs of peaks in a particular doublet to be equal. The 1% and 99% confidence limits for the χ^2 value which is used as a measure of the goodness of a computer-fit are 570 and 424 for a 6-peak fit and 566 and 420 for an 8-peak fit. In order for this χ^2 value to be used as an indicator of both the validity of the model used and the extent of disorder within the structure, all spectra were recorded to a suitably high background count of 7–8 $\times$ 10^6 (Johnston and Cardile, 1985a). The experimental and computer-fitted spectra are presented in Figures 1, 2, 3, and 5; the computer-fitted parameters are given in Table 2.

RESULTS AND DISCUSSION

In general, the computer-fitted data obtained from the spectra of all the clay samples showed two prominent Fe^{3+} doublets with δ and Δ values of approximately 0.38, 0.25 (inner doublet) and 0.38, 0.6 (outer doublet) mm/sec, respectively, assigned to F^{3+} in the two distinct cis-$FeO_4(OH)_2$ octahedral sites (Table 2 and Figures 1, 2, 3, and 5) (Johnston and Cardile, 1985a). The precise δ and Δ values, however, and the widths and areas of these respective doublets differed between samples. Also, for most spectra a less intense Fe^{3+} doublet with δ and Δ values of about 0.18 and 0.44 mm/sec, attributed to Fe^{3+} replacing (Si,Al) in the tetrahedral sites, was fitted. This resonance usually contributed 5–10% to the overall area of the experimental spectrum. Additional doublets with as much as 5% of the overall area were computer-fitted to the spectra of the untreated samples only.

The spectra for untreated and Ca-saturated SPO nontronite (Figure 1) were similar to those presented earlier for nontronite from Garfield, Washington (GAR) (Johnston and Cardile, 1985a). The χ^2 value of 3567 for the 8-peak fit defining two octahedral, one tetrahedral, and one interlayer Fe^{3+} doublets was above the upper confidence level and was indicative of disorder in the structure of this SPO nontronite although, as discussed below, some partial magnetic relaxation was also present. The effect of Ca-saturation which displaced the interlayer Fe^{3+} tended to order the structure, and hence the χ^2 value of 762 was lower. A similar result was obtained for the GAR nontronite (Johnston and Cardile, 1985a) and indeed suggested that much of the disorder is associated with the nature and location of the interlayer cation. The relative peak areas (Table 2) show that for the untreated SPO sample the outer octahedral doublet comprised 60% of the overall absorption, the inner octahedral doublet 28%, the tetrahedral doublet 8%, and the interlayer doublet 4%. When the sample was saturated with Ca, these outer, inner octahedral, and tetrahedral doublets comprised 80%, 13%, and 7% of the overall absorption, respectively. Because Ca-saturation is unlikely to cause displacement of Fe^{3+} within the octahedral layer (Johnston and Cardile, 1985a), it is apparent that the interlayer cation influences the recoilless fraction of Fe^{3+} in the cis-octahedral sites. This influence again confirms the suggestion made by Johnston and Cardile (1985a), based upon a study of the Garfield nontronite, that the interlayer cation may give rise to two distinct electric field gradients for iron in the cis-$FeO_4(OH)_2$ sites and hence the two overlapping Fe^{3+} doublets noted here.

The spectrum for untreated SPO nontronite recorded at 83°K and superimposed on the room temperature spectrum (Figure 1a) showed considerable line broadening, particularly at the base of the absorption. The 83°K spectrum could not be computer-fitted satisfactorily and hence indicated that the broadening was due to the initial stages of magnetic relaxation, arising from long range –Fe–O–Fe– type interactions within the structure. This broadening is interesting as 83°K is a high temperature for the onset of magnetic ordering in silicates. It is possible that the sample contained some surface adsorbed superparamagnetic iron oxides which could show incipient magnetic order at this temperature. We have recently measured the Mössbauer spectra at 4.2°K for untreated and Ca-saturated SPO non-

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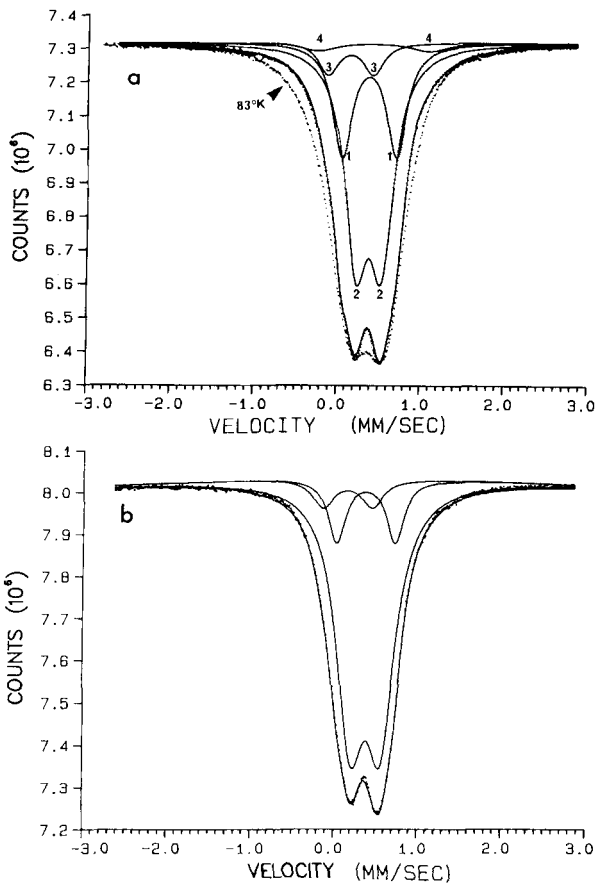


Figure 1. Experimental and computer-fitted Mössbauer spectra for the Spokane County, Washington (SPO), nontronite: (a) untreated room temperature with the experimental 83°K spectrum (outer envelope of points) superimposed. Doublets: 1 = outer octahedral Fe^{3+}, 2 = inner octahedral Fe^{3+}, 3 = tetrahedral Fe^{3+}, 4 = interlayer Fe^{3+}. (b) Ca-saturated, room temperature.

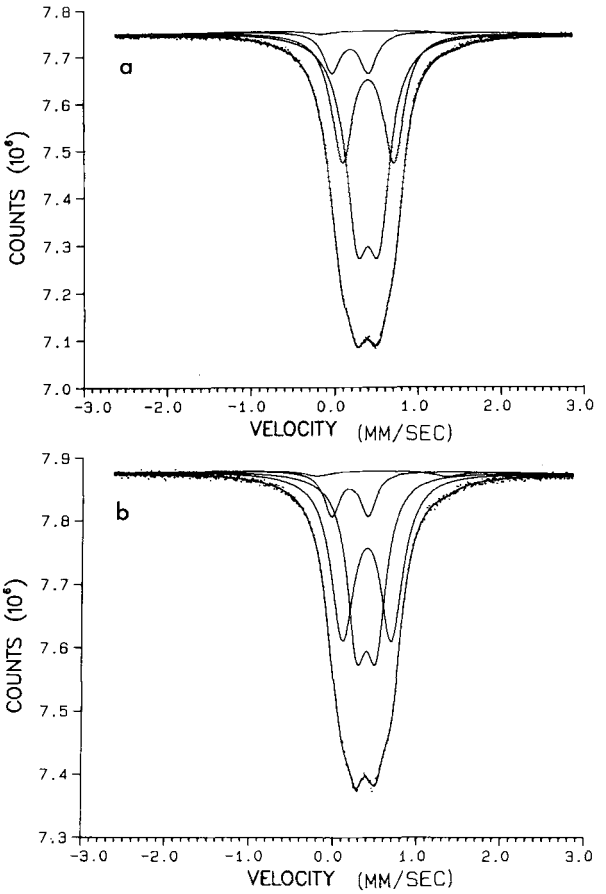


Figure 2. Experimental and computer-fitted Mössbauer spectra for (a) untreated, (b) Ca-saturated Manito, Washington (MAN), nontronite.

tronite, however, and both samples produced a complex spectrum with a number of closely overlapping sextets thereby verifying the above suggestion that at least some of the magnetic ordering is associated with the nontronite structure itself (Johnston and Cardile, 1985b).

The Mössbauer spectra of the untreated and Ca-saturated MAN nontronite are shown in Figure 2, and the computer-fitted parameters are listed in Table 2. The χ^2 value of 609 for the untreated MAN sample was slightly lower than that of the Ca-saturated MAN nontronite (615), but both values were close to the upper confidence limit, suggesting that the MAN nontronite is more ordered than the SPO nontronite. The minor peaks at −0.18 and 1.40 mm/sec occur at slightly different positions from those of the interlayer resonance in the SPO nontronite. These are in fact the inner two peaks of a finely divided iron oxide, adsorbed onto the surface of the clay particles. This iron oxide coating was verified by recording the spectrum over a wider velocity range. Similarly, no such iron oxide coatings were observed on the other nontronites. This oxide coating was not removed with Ca-saturation of the MAN nontronite sample (Figure 2).

The Mössbauer spectrum of the untreated BIN nontronite showed two distinct Fe^{2+}-doublet resonances, as well as the inner and outer octahedral Fe^{3+} doublets (Figure 3a). The δ and Δ values (Table 2) for both Fe^{2+} doublets are consistent with those commonly observed for Fe^{2+} in octahedral coordination in silicate structures (e.g., Bancroft, 1973), suggesting that the Fe^{2+} was located in the octahedral $FeO_4(OH)_2$ sites within the nontronite structure. Upon Ca-saturation, however, both Fe^{2+} doublets were removed (Figure 3b) confirming that the Fe^{2+} was in the interlayer instead and at least two distinct interlayer sites are present. Diamant *et al.* (1982) reported interlayer Fe^{2+} in montmorillonite with values of δ = 1.04(3) and Δ = 3.12 (3) mm/sec, which differ from those of δ = 1.09 (1) and

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Table 2. Computer-fitted Mössbauer spectral data for nontronites.

Nontronite sample[1]	Fe (wt. %)	χ^2	Inner octahedral Fe^{3+} doublet δ (mm/sec)	Δ (mm/sec)	Width (mm/sec)	Area (%)	Outer octahedral Fe^{3+} doublet δ (mm/sec)	Δ (mm/sec)	Width (mm/sec)	Area (%)
Ut-SPO		3567	0.378 (3)	0.307 (3)	0.34 (1)	60 (1)	0.376 (3)	0.655 (3)	0.29 (1)	28 (1)
Ca-SPO	29.20	762	0.374 (5)	0.362 (5)	0.42 (1)	80 (1)	0.366 (6)	0.701 (6)	0.25 (1)	13 (1)
Ut-MAN		609	0.383 (6)	0.259 (6)	0.33 (1)	54 (3)	0.388 (7)	0.614 (7)	0.30 (1)	36 (1)
Ca-MAN	25.06	615	0.384 (6)	0.231 (6)	0.28 (1)	40 (2)	0.391 (8)	0.583 (8)	0.33 (6)	49 (1)
Ut-BIN		570	0.364 (3)	0.263 (3)	0.35 (1)	59 (1)	0.361 (4)	0.641 (4)	0.32 (1)	34 (1)
Ca-BIN	20.05	563	0.370 (5)	0.242 (5)	0.32 (1)	51 (1)	0.371 (6)	0.619 (6)	0.32 (1)	45 (1)
Li-CAL	34.95	589	0.386 (6)	0.275 (6)	0.40 (1)	61 (2)	0.386 (6)	0.613 (6)	0.31 (1)	29 (2)
Na-KOE	33.39	645	0.387 (4)	0.315 (4)	0.33 (1)	54 (1)	0.383 (5)	0.630 (5)	0.27 (1)	25 (1)
Ca-WOD	28	548	0.369 (5)	0.253 (5)	0.30 (1)	47 (1)	0.371 (7)	0.558 (7)	0.31 (1)	35 (1)

Nontronite sample[1]	Tetrahedral Fe^{3+} doublet δ (mm/sec)	Δ (mm/sec)	Width (mm/sec)	Area (%)	Interlayer Fe^{2+}/Fe^{3+} doublet[2] δ (mm/sec)	Δ (mm/sec)	Width (mm/sec)	Area (%)
Ut-SPO	0.147 (6)	0.546 (6)	0.29 (1)	8 (1)	0.42 (2)	1.34 (2)	0.54 (4)	4.2 (3)
Ca-SPO	0.146 (10)	0.587 (10)	0.32 (1)	7 (1)	—	—	—	—
Ut-MAN	0.175 (7)	0.436 (7)	0.24 (1)	9 (1)	—	—	—	—
Ca-MAN	0.179 (8)	0.432 (8)	0.23 (1)	9 (1)	—	—	—	—
Ut-BIN	—	—	—	—	1.00 (1) 1.17 (6)	2.23 (1) 2.61 (6)	0.25 (1) 0.29 (4)	5.4 (2) 1.5 (3)
Ca-BIN	0.15 (1)	0.44 (1)	0.23 (2)	4 (1)	—	—	—	—
Li-CAL	0.208 (7)	0.506 (7)	0.27 (1)	10 (1)	—	—	—	—
Na-KOE	0.192 (4)	0.516 (4)	0.27 (1)	21 (1)	—	—	—	—
Ca-WOD	0.187 (7)	0.471 (7)	0.31 (1)	18 (1)	—	—	—	—

[1] Ut = untreated; Ca = Ca-saturated; Li = Li-saturated; Na = Na-saturated.
[2] Fe^{3+} for SPO and MAN nontronites, Fe^{2+} for BIN nontronite.
The figures in parentheses are one standard deviation.

Δ = 2.76 (2) mm/sec for Fe^{2+} in the octahedral sites in that montmorillonite. Helsen and Goodman (1983) also reported values of δ = 1.38 and Δ = 3.36 mm/sec for exchanged or interlayer Fe^{2+} in montmorillonite and hectorite. They suggested that this large Δ value indicates that the Fe^{2+} more closely resembles a Fe^{2+}(aq) ion, rather than Fe^{2+} in octahedral oxygen coordination in a silicate structure. Both groups of workers reported only one Fe^{2+} doublet. The values of Δ = 2.61 (6) and 2.23 (1) mm/sec (Table 2) for such interlayer Fe^{2+} in the BIN nontronite are lower than those observed for montmorillonite, a result which is not unexpected as the Δ values for Fe^{3+} in nontronites are also generally lower than those for montmorillonites (e.g., Rozenson and Heller-Kallai, 1977; Johnston and Cardile, 1985a).

In a study of the stacking order of a Cs-saturated smectite Besson *et al.* (1983b) suggested that the Cs could be located in two distinct interlayer sites, the pseudo-hexagonal cavity (site 1, Figure 4) formed by the linked $(Si,Al)O_4$ tetrahedra and a site adjacent to it. Although they did not describe this latter site precisely, it could lie directly above the (Si,Al) atoms in the tetrahedral layer (site 2, Figure 4). It is probable that the Fe^{2+} in both the interlayer sites is hydrated and that the Fe^{2+}(aq) ion is H-bonded to the oxygens in the tetrahedral layer. Such unequivocal predictions, however, are difficult to make because of inherent disorder and the probable presence of other ions in the interlayer. Interlayer Fe^{3+} was not detected in the BIN nontronite, from which it is concluded that the untreated form of this nontronite must have been in contact with a Fe^{2+}-containing solution in nature, under reducing conditions.

Furthermore, it was not possible to computer-fit a doublet defining Fe^{3+} in the tetrahedral sites to the spectrum for the untreated BIN nontronite, but such a doublet was fitted to the Ca-saturated BIN sample (Figure 3). It is very unlikely that the Ca-saturation produced a migration of Fe^{3+} into the tetrahedral sites. Rather, the complex effect of computer-fitting two interlayer Fe^{2+} doublets in which the low-velocity peaks overlap almost completely with that of the tetrahedral Fe^{3+} resonance in question, as well as the two much more intense octahedral Fe^{3+} doublets, simply precluded locating such a tetrahedral Fe^{3+} doublet. When the model was simplified by displacing the Fe^{2+} with Ca-saturation, the tetrahedral Fe^{3+} doublet was distinguished in the computer-fitting procedure. Also, as noted above, there are marked differences in the relative intensities of the computer-fitted cis-octahedral Fe^{3+} doublets between the respective spectra for the untreated and Ca-saturated BIN nontronites (Figure 3, Table 2). These differences further emphasize the need for caution when attempting to interpret such computer-fitted spectra rigorously for complex silicates and

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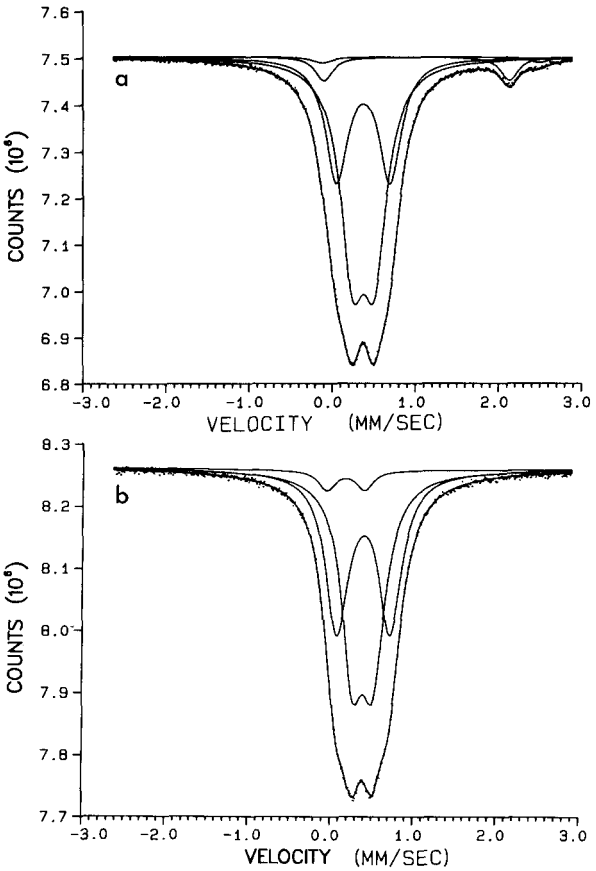


Figure 3. Experimental and computer-fitted Mössbauer spectra for (a) untreated, (b) Ca-saturated Bingham Canyon, Utah (BIN), nontronite.

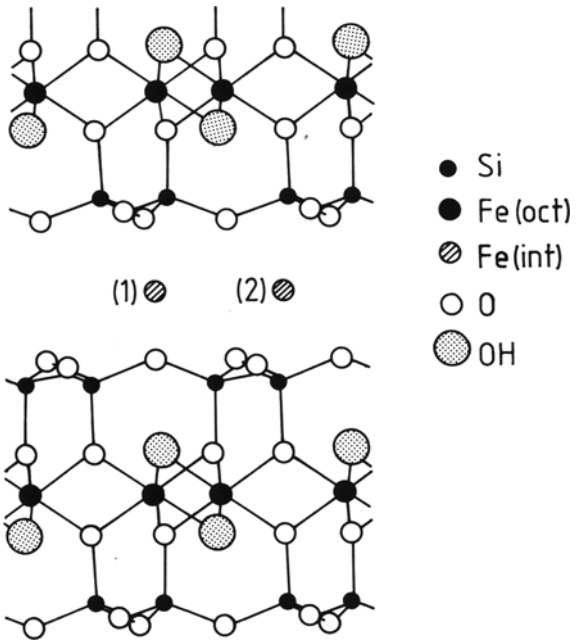


Figure 4. Nontronite structure showing the (1) pseudo-hexagonal, (2) adjacent interlayer sites (based on a computer-generated drawing courtesy of Dr. I. W. M. Brown, DSIR, Lower Hutt, New Zealand).

indeed may lead to a rethinking of the interpretation of the Mössbauer spectra of such silicates.

The Li-saturated CAL and Na-saturated KOE nontronites have the highest iron contents (34.95 and 33.39 wt. %, respectively) of the samples examined. On a conventional basis they have insufficient Al and Si to fill the tetrahedral sites, suggesting the presence of tetrahedral Fe^{3+} (Table 1). The computer-fitted Mössbauer spectra (Figures 5a and 5b) for these show that the tetrahedral doublet contributed 21% to the overall absorption area for the KOE nontronite, but only 10% to the CAL nontronite. Because the total Fe contents for the samples were similar, the only real differences between these two nontronites were that the CAL nontronite had Li as the interlayer cation (d(001) = 12.67 Å) and the KOE nontronite was Na-saturated (d(001) = 14.46 Å). The difference in the Mössbauer peak areas, particularly for the tetrahedral Fe^{3+} resonance, again indicates the influence of the interlayer cations on the Mössbauer resonances for structural Fe in such silicates. These d(001) values are smaller than that of the Ca-saturated samples (d(001) = 15.4 Å) and suggest that Na and Li interlayer cations have a greater such influence on the Mössbauer resonances than interlayer Ca. No interlayer Fe was detected in these two nontronites.

The WOD nontronite was mixed with ~30% silica, mainly as cristobalite, and hence its composition could not be determined precisely. By recalculating the SiO_2 content of this sample to the mean of the other nontronites, however, an approximate Fe content of 28% was obtained, intermediate between that of the GAR and SPO nontronites (Table 1). The spectrum of the Ca-saturated sample showed only octahedral- and tetrahedral-Fe^{3+} doublets (Figure 5c). Because the 18% contribution of the tetrahedral doublet to the overall absorption was significantly larger than that observed here for the other Ca-saturated nontronites (Table 2), some silica was probably present in the interlayer of the WOD sample and thus influenced the tetrahedral Fe^{3+} resonance. Although this hypothesis is difficult to verify, silica was introduced into the interlayer of a smectite by Endo *et al.* (1980).

The χ^2 values for all the nontronites studied here, with the exception of the SPO sample (Table 2), were generally just above the upper confidence level of 570 for a 6-peak fit and 566 for an 8-peak fit. If the computer-fitted model is correct and the χ^2 value can be used as measure of the structural order, it appears that the BIN and MAN nontronites are reasonably well ordered (Johnston and Cardile, 1985a).

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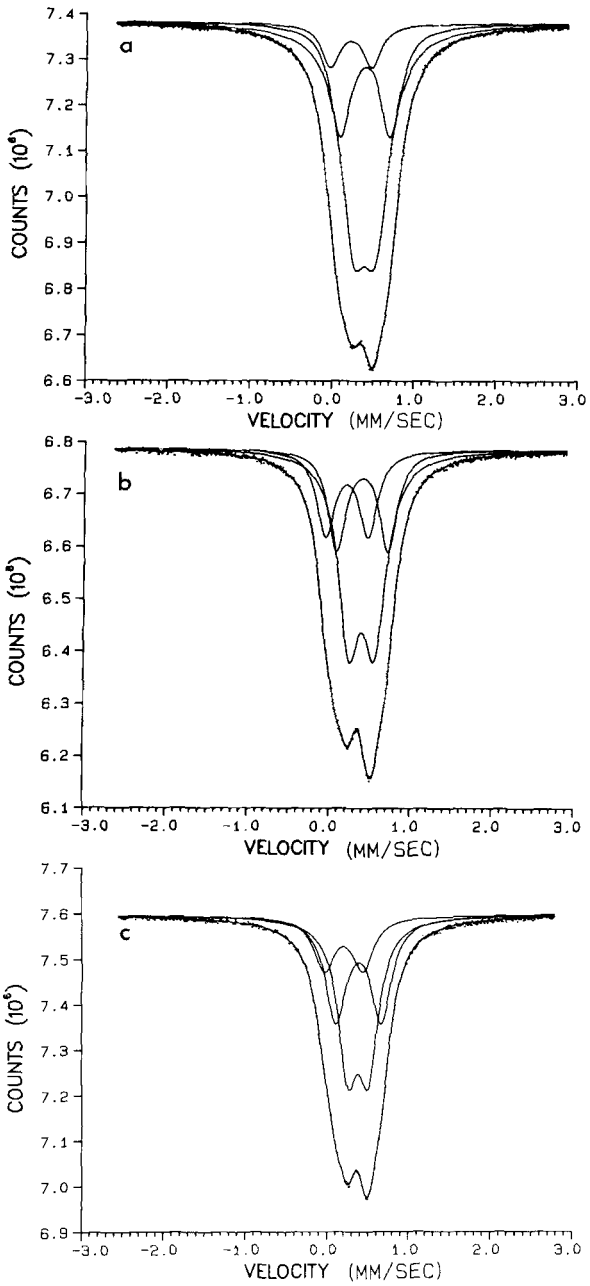


Figure 5. Experimental and computer-fitted Mössbauer spectra for (a) Li-saturated Panamint Valley, California (CAL), (b) Na-saturated Koegas, South Africa (KOE), and (c) Ca-saturated Woody, California (WOD), nontronites.

Some structural disorder was present in the Ca-saturated SPO nontronite, and partial magnetic relaxation at 83°K is evident for the untreated sample.

CONCLUSION

From the data presented here and earlier (Johnston and Cardile, 1984), no definitive relation is apparent between the distribution of Fe within the various octahedral, tetrahedral, and interlayer sites and the Fe content of the nontronite. It is clear, however, that the interlayer cation has a significant effect on Mössbauer resonances of Fe in both the cis-octahedral and the tetrahedral sites, thus rendering the use of computer-fitted Mössbauer spectral peak areas inappropriate for the measurement of the iron-site distribution within these smectites. It seems that, for the BIN nontronite at least, the interlayer cations may be located in two distinct interlayer sites. Interlayer iron usually exists as Fe^{3+}, but in one of the nontronites examined, it was present as Fe^{2+}.

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REFERENCES

Bancroft, G. M. (1973) *Mössbauer Spectroscopy: An Introduction for Inorganic Chemists and Geochemists:* McGraw-Hill, London, 252 pp.

Besson, G., Bookin, A. S., Dainyak, L. G., Rautureau, M., Tsipursky, S. I., Tchoubar, C., and Drits, V. A. (1983a) Use of diffraction and Mössbauer methods for the structural and crystallochemical characterisation of nontronites: *J. Appl. Cryst.* **16,** 374–383.

Besson, G., Glaeser, R., and Tchoubar, G. (1983b) Le césium révélateur de structure des smectites: *Clay Miner.* **18,** 11–19.

Diamant, A., Pasternak, M., and Banin, A. (1982) Characterization of adsorbed iron in montmorillonite by Mössbauer spectroscopy: *Clays & Clay Minerals* **30,** 63–66.

Endo, T., Mortland, M. M., and Pinnavaia, T. J. (1980) Intercalation of silica in smectite: *Clays & Clay Minerals* **28,** 105–110.

Goodman, B. A. (1978) The Mössbauer spectra of nontronites: consideration of an alternative assignment: *Clays & Clay Minerals* **26,** 176–177.

Goodman, B. A., Russell, J. D., Fraser, A. R., and Woodhams, F. W. D. (1976) A Mössbauer and infrared spectroscopic study of the structure of nontronite: *Clays & Clay Minerals* **24,** 53–59.

Helsen, J. A. and Goodman, B. A. (1983) Characterisation of iron(II) and iron(III)-exchanged montmorillonite and hectorite using the Mössbauer effect: *Clay Miner.* **18,** 117–125.

Johnston, J. H. and Cardile, C. M. (1985a) Iron sites in nontronite and the effect of interlayer cations from Mössbauer spectra: *Clays & Clay Minerals* **33,** 21–30.

Johnston, J. H. and Cardile, C. M. (1985b) Magnetic ordering of a nontronite at 4.2°K: *Clays & Clay Minerals* (in press).

Rozenson, I. and Heller-Kallai, L. (1977) Mössbauer spectra of dioctahedral smectites: *Clays & Clay Minerals* **25,** 94–101.

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